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Publication Date

1960

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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ABSTRACT

The operator-equivalent method was employed to calculate the theoretical splitting of electronic energy levels 3P_2 , 1D_2 , 3F_2 , 3F_3 , 3F_4 , 1G_4 , and 3H_6 in $Tm(C_2H_5SO_4)_3 \cdot 9 H_2O$. Intermediate field corrections were made to α , β , and γ . A first-order perturbation treatment on $Tm^{+3} (4f^{12})$ in C_{2h} symmetry, using crystal-field parameters $A_2^0 \langle r^2 \rangle = 13 \text{ cm}^{-1}$, $A_4^0 \langle r^4 \rangle = -80 \text{ cm}^{-1}$, $A_6^0 \langle r^6 \rangle = -32 \text{ cm}^{-1}$, and $A_6^6 \langle r^6 \rangle = 300 \text{ cm}^{-1}$, predicts the position of the crystal quantum states in reasonable agreement with experiment.

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INTRODUCTION

In a $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ single crystal, where the Tm^{+3} configuration is $4f^{12}$, the perturbing influence of the water and ethylsulfate groups on the energy-level system of the free ion can be calculated by expanding the crystal-field electric potential in a series of spherical harmonics. A first-order perturbation treatment is possible since the crystal field splitting of the various electronic levels is of the order of 100 cm^{-1} , whereas the spin orbit splitting between adjacent levels is generally greater than 1000 cm^{-1} . The work of Ketelaar has shown that the point symmetry at the metal-ion site in rare earth ethylsulfates is predominately C_{3h} .¹ Johnsen² and the present authors³ have found C_{3h} point symmetry to be consistent with the interpretation of the $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ absorption spectra. However, a few transitions were observed that are forbidden in C_{3h} symmetry but are allowed in C_{3v} symmetry. The theoretical splitting of $^3\text{H}_6$, $^3\text{F}_4$, $^3\text{F}_3$, $^3\text{F}_2$, $^1\text{G}_4$, $^1\text{D}_2$, and $^3\text{P}_2$ levels presented here is based on the experimental work of these investigators.

CALCULATION OF INTERMEDIATE-FIELD OPERATOR EQUIVALENTS

The potential energy of a $4f$ electron in the electrostatic field of the lattice is taken to be

$$A_2^0 (3 Z^2 - r^2) + A_4^0 (35 Z^4 - 30 Z^2 r^2 + 3 r^4) + A_6^0 (231 Z^6 - 315 Z^4 r^2 + 105 Z^2 r^4 - 5 r^6) + A_6^6 (x^6 - 15 x^4 y^2 + 15 x^2 y^4 - y^6).$$

The contribution to the free- Tm^{+3} Hamiltonian consists of two expressions of this form, corresponding to the two $4f$ electron "holes". The

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

quantities A_n^m are characteristic of the lattice and appear with the corresponding quantities $\langle r^n \rangle$, the mean value of r^n for a single $4f$ electron.

As Stevens has shown,⁴ within a given manifold of J the matrix elements of the potential form V_n^m associated with the parameter A_n^m are related to the matrix elements of certain angular-momentum operators through a factor $\theta_n \langle r^n \rangle$. Here θ_n is the so-called "operator equivalent" factor, usually written as α , β , and γ for $n = 2, 4$, and 6 . This theory has been generalized by Elliott *et al.* for all rare earth ions.⁵ Judd has given the equations for evaluating the pure L-S operator equivalent for $\text{Pr}^{+3}(4f^2)$.⁶ He has tabulated these values for 3H_4 , 1G_4 , 3F_4 , 3F_3 , 1D_2 , 3P_2 , and 3P_1 in the same paper with the crystal-field-splitting results for Pr^{+3} in LaCl_3 . For $\text{Tm}^{+3}(4f^{12})$, the L-S α , β , and γ may be calculated from the Pr^{+3} set of equations. The only difference will be a change in sign. However, L-S coupling breaks down in Tm^{+3} , and it is necessary to consider intermediate coupling effects on the L-S operator equivalents.

In an earlier paper³ the electronic energy levels for Tm^{+3} in the intermediate field were obtained from a plot of E/F_2 vs χ , where $\chi = \zeta/F_2$, ζ is the spin orbit parameter used by Spedding,⁷ and F_2 is a Slater integral. The best fit of theory to experiment was obtained at $\chi = 3$. The eigenvectors at $\chi = 3$ for 3H_4 , 3F_4 , 1G_4 , and 3F_2 , 3P_2 , 1D_2 , used in calculating α , β , and γ in the intermediate field were obtained from an IBM-650 program. The eigenvectors for 3H_6 and 1I_6 were calculated by hand using Spedding's equations. Table I includes values of operator equivalents for $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ with intermediate-field corrections in brackets.

Suppose we wish to calculate α , β , and γ for 1G_4 in an intermediate field at $\chi = 3$. In a $4f^{12}$ configuration there are three $J = 4$ levels. We write

$$\| ^1G'_4 \rangle = 0.6119 \| ^3H_4 \rangle + 0.7260 \| ^1G_4 \rangle - 0.3137 \| ^3F_4 \rangle, \quad (1)$$

where 0.6119, 0.7260, and -0.3137 are the corresponding eigenvectors, and $\| ^1G'_4 \rangle$ corresponds to the intermediate field 1G_4 . Now we have

$$\begin{aligned}
\langle {}^1G'_4 \parallel \begin{matrix} \alpha \\ \beta \\ \gamma \end{matrix} \parallel {}^1G'_4 \rangle &= (0.6119)^2 \langle {}^3H_4 \parallel \begin{matrix} \alpha \\ \beta \\ \gamma \end{matrix} \parallel {}^3H_4 \rangle + (0.7260)^2 \langle {}^1G_4 \parallel \begin{matrix} \alpha \\ \beta \\ \gamma \end{matrix} \parallel {}^1G_4 \rangle \\
&+ (0.3137)^2 \langle {}^3F_4 \parallel \begin{matrix} \alpha \\ \beta \\ \gamma \end{matrix} \parallel {}^3F_4 \rangle - 2(0.3137)(0.6119) \langle {}^3H_4 \parallel \begin{matrix} \alpha \\ \beta \\ \gamma \end{matrix} \parallel {}^3F_4 \rangle \quad (2)
\end{aligned}$$

There will be no cross terms involving 1G_4 with 3F_4 and 3H_4 , since matrix elements between different spin states are zero. Each of the pure L-S operator equivalents in Eq. (2) can be evaluated from the equations given by Judd.⁶ It is possible to factor out 1G_4 , L-S α , β , and γ expressions from the right-hand side of Eq. (2), which leaves a sum of numbers that denotes the importance of intermediate-field corrections to the L-S operator-equivalent values. In this way, 3F_4 , 3F_2 , 3P_2 , 1D_2 , and 3H_6 operator equivalents were calculated. The 3P_1 , 3F_3 , and 3H_5 operator equivalents are not affected by spin-orbit interaction.

SELECTION OF PARAMETERS

Having found α , β , and γ for a particular level, we can now express the crystal splitting in terms of parameters $A_n^m \langle r^n \rangle$. These parameters were defined earlier. The values that these parameters can assume must be consistent with the point symmetry at the rare-earth ion in the lattice.

In addition to containing some physical significance as a scale factor for the crystalline electric potential, A_n^m is also the repository for errors due to neglect of configuration interaction and interactions between crystal quantum states of one J level with those of a nearby J level. Since configuration interaction has greater effect on J levels in the ultraviolet than in the infrared, the $A_n^m \langle r^n \rangle$ parameters can not be expected to be really constant in going from 3H_6 to 3P_2 , some $38,000 \text{ cm}^{-1}$ away. Likewise, somewhat different parameter values are needed if a simultaneous perturbation treatment is carried out on the 3F_2 , 3F_3 , and 3F_4 levels and if a general second-order perturbation treatment is carried out.

If we neglect the effects mentioned in the preceding paragraph, the structure of 3P_1 (split into 2 sublevels $\mu = 0, \pm 1$) gives at once a preliminary value for $A_2^0 \langle r^2 \rangle$. Unfortunately, our photographic plates unambiguously confirmed only the position of the $\mu = \pm 1$ sublevel in 3P_1 . Another line appearing in both σ and π polarization with a line width of

some 10 cm^{-1} may have been 2 lines close together. More careful polarization experiments, in which the σ and π spectra are taken as a function of the rotation of the crystal, are necessary to confirm the actual energy value of the splitting. Parameters $A_6^6 < r^6 >$ and $A_6^0 < r^6 >$ were chosen so as to give the proper splitting of the $\mu = 3$ and $\mu = \pm 2$ sublevels in 3F_4 , 1G_4 , and 3H_6 . Parameter $A_4^0 < r^4 >$ was chosen so as to give reasonable splitting of the 3P_2 , 3F_2 , and 3H_6 levels. The best over-all fit for this first-order perturbation treatment was obtained by using $A_2^0 < r^2 > = 13 \text{ cm}^{-1}$, $A_4^0 < r^4 > = -80 \text{ cm}^{-1}$, $A_6^0 < r^6 > = -32 \text{ cm}^{-1}$, and $A_6^6 < r^6 > = 300 \text{ cm}^{-1}$.

FITTING TO EXPERIMENTAL DATA

A. The 3H_6 Level (see Fig. 1)

The theoretical predictions for $\mu = 0, \pm 1, 3$ are in good agreement with those crystal quantum states reported by experiment. The prediction of additional states between ± 1 and 3 has led us to restudy our plates. Our reported analysis included only those intense lines in which polarization was complete.³ As many as 3 or 4 weak lines appear between those due to transitions from the ± 1 and 3, but these are not well polarized. These lines may be due to sublevels $\mu = 0', \pm 1'$, and $\pm 2'$ in 3H_6 as the theory predicts or satellite levels, but our experiments cannot really confirm this. Forbidden transitions observed in 3P_2 , 1D_2 , and 1G_4 may also confirm these predicted states in the 3H_6 level.

B. The 3F_4 Level (see Fig. 2)

The splittings of the $\mu = \pm 2$ and 3 are in reasonable agreement with experiment. However, the presence of the 3F_3 some 200 cm^{-1} away will cause certain states to be depressed more than others. This may explain the relative position of the theoretical value of $\mu = \pm 1$.

C. The 3F_3 and 3F_2 Levels (see Figs. 3 and 4)

Since 3F_3 and 3F_2 are separated by 400 cm^{-1} , a simultaneous perturbation treatment is necessary in order to get better fit. Such a treatment may reverse the positions $\mu = \pm 1$, $\mu = \pm 2$ in 3F_2 , now given as a result of first-order methods. As yet, $\mu = 0$ has not been reported for either of these levels.

D. The 1G_4 Level (see Fig. 2)

The splitting between the lower $\mu = 3$ and $\mu = \pm 1$, between $\mu = \pm 2$ and $\mu = \pm 1$, and between $\mu = \pm 1$ and lower $\mu = \pm 2$ fits that found by experiment. The experimental positions of both $\mu = 3$ sublevels are reasonably well established. The theoretical value of upper $\mu = 3$ cannot be brought into better agreement by this present treatment. A slightly different set of parameters, $A_2^0 < r^2 > = 13 \text{ cm}^{-1}$, $A_4^0 < r^4 > = -80 \text{ cm}^{-1}$, $A_6^0 < r^6 > = -20 \text{ cm}^{-1}$, and $A_6^6 < r^6 > = 200 \text{ cm}^{-1}$ gives the following somewhat better agreement: $\mu \pm 2 = -79 \text{ cm}^{-1}$, $\mu \pm 1 = -50 \text{ cm}^{-1}$, $\mu \pm 2' = 23 \text{ cm}^{-1}$, $\mu 3 = 101 \text{ cm}^{-1}$, $\mu 3' = 166 \text{ cm}^{-1}$.

That a slightly different set of parameters fits theory better to data may be due to increased importance of configuration interaction on excited levels. However, the internal inconsistency within the 1G_4 may be due to interactions between crystal quantum states of 1G_4 with those in 3F_2 , 3F_3 , and 1D_2 .

The 1D_2 Level (see Fig. 4)

The poor agreement can be partially remedied by considering interaction of 1D_2 with 1I_6 . Our plates reveal lines between 3P_1 and 3P_0 and to the red of 3P_0 as possibly due to the 1I_6 . The energy of 1I_6 above 1D_2 was taken to be 6000 cm^{-1} . Even when the total matrix of the crystal field interaction between 1D_2 and 1I_6 is considered, it is impossible to obtain good agreement with 1I_6 this far removed from 1D_2 .

Judd has also obtained a poor fit for 1D_2 in the analysis of PrCl_3 ($\text{Pr}^{+3}, 4f^2$).⁶ Although configuration interaction is known to be important for 1D_2 , it is difficult to see in detail why this poor agreement occurs again in Tm^{+3} .

The 3P_2 Level (see Fig. 4)

Actually good agreement exists between theory and experiment. The experimental error in measuring the broad lines in the ultraviolet is some 13 cm^{-1} in magnitude.

Table I

Operator Equivalents in the Intermediate Field, $Tm^{+3} (4f^{12})$						
Level	$\langle J \ \alpha \ J \rangle$		$\langle J \ \beta \ J \rangle$		$\langle J \ \gamma \ J \rangle$	
3P_1	$\frac{1}{5}$	[1.000]	0		0	
3P_2	$\frac{-1}{15}$	[1.095]	$\frac{-4}{7.27}$	[0.629] ^a	0	
1D_2	$\frac{-22}{15.21}$	[0.678]	$\frac{-4}{7.27}$	[-0.105]	0	
3F_2	$\frac{-8}{21.15}$	[1.636]	$\frac{2}{7.81}$	[-1.859]	0	
3F_3	$\frac{-1}{90}$	[1.000]	$\frac{1}{45.99}$	[1.000]	$\frac{1}{39.99}$	[1.000]
3F_4	$\frac{-1}{126}$	[-1.357]	$\frac{1}{45.77}$	[1.527]	$\frac{-1}{13.63.99}$	[5.945]
1G_4	$\frac{2}{11.35}$	[1.799]	$\frac{46}{11.45.77}$	[0.866]	$\frac{4}{13.33.77}$	[0.537]
1I_6	$\frac{2}{99}$	[0.995]	$\frac{-4}{11.15.99}$	[0.984]	$\frac{2}{13.33.21.99}$	[0.967]
3H_6	$\frac{1}{99}$	[1.010]	$\frac{8}{3.11.1485}$	[0.976]	$\frac{-5}{13.33.2079}$	[0.986]

^aThe pure L-S operator equivalent, β , is zero for 3P_2 , since the corresponding Racah coefficient is zero. However, if we allow for intermediate coupling effects, the entry becomes $(-4/7.27)$ [0.629].

ACKNOWLEDGMENT

We wish to express our appreciation to Dr. B. R. Judd for his valuable discussion and suggestions during the writing of this paper. We also extend thanks to Mr. J. D. Axe who checked several of the calculations.

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μ	calc (cm^{-1})	μ	obs (cm^{-1})
3	151		
± 2	108	± 2	231
3	51	3	195
± 1	-4		
± 2	-6		
0	-30		
0	-37		
± 1	-96	± 1	33
0	-130	0	0

MU-19219

3F_4

1G_4

μ	calc (cm^{-1})	μ	obs (cm^{-1})	μ	calc (cm^{-1})	μ	obs (cm^{-1})
± 2	102	± 2	12763	3	199		
3	49	± 1	12720			3	21379
		3	12704	3	101	3	21341
± 1	-18	± 2	12649				
± 2	-28			± 2	12	± 2	21279
3	-62	3	12586			0	21255
0	-99			0	-40		
				± 1	-50	± 1	21191
				± 2	-92	± 2	21168

MU-19220

3F_3

μ	calc (cm ⁻¹)	μ	obs (cm ⁻¹)
0	25	3	14487
3	21	± 2	14486
± 2	17		
		± 1	14466
± 1	-22		
3	-35	3	14407

MU-19221

3P_2

1D_2

3F_2

μ	calc (cm^{-1})	μ	obs (cm^{-1})	μ	calc (cm^{-1})	μ	obs (cm^{-1})	μ	calc (cm^{-1})	μ	obs (cm^{-1})
0	82			± 1		± 1	27971				
± 2	7	± 2	38140	± 1	22	± 2	27900	0	41	± 2	15106
				0	-12	0	27876	± 1	3	± 1	15079
± 1	-48				-18				-24	± 2	
		± 1	38060								

MU-19222